Growth of Silicon Bicrystals by the Dash Pedestal-Method

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ABSTRACT

Silicon bicrystals are grown in an inert atmosphere avoiding quartz crucibles. The oxygen content of the bicrystals is below the limit of detection with the 9μ absorption line. The Dash pedestal method is modified, and the bicrystals are pulled from the melt by means of a "bi-seed" which contains a small angle grain boundary. A float zone scanner is converted into a crystal grower. A "drill press"-etching apparatus facilitates the etching of the seed crystals to a needle-like shape with the grain boundary in the center of the 0.1 mm diameter of the tip.

Small angle grain boundaries consist of a regular array of edge dislocations (1-3). Bicrystals with such boundaries are an excellent tool to investigate dislocations. From the result of grain boundary experiments one can draw conclusions about the behavior of isolated dislocations.

Silicon bicrystals have been studied in the past (4-8). Enhanced diffusion along small angle grain boundaries in silicon has been found in this laboratory (5). Phonon drag measurements in silicon grain boundary specimens have been carried out by Hubner and Shockley (6), and light emission at high voltage from a grain boundary junction has been observed by Goetzberger and Stephens (7). All these experiments were made with oxygen-rich bicrystals grown from a quartz crucible by the Czrochralski method (9). It is, however, not well known what role oxygen plays in the behavior of silicon crystals together with dislocations. Hooper and Queisser (8) recently found a strong influence of heat treatment on the photoresponse of Si bicrystals. They assumed that oxygen particularly accounts for these effects. For further studies it is, therefore, desirable to have both oxygen-rich and oxygen-free silicon grain boundary crystals available. All bicrystals obtained by the standard crucible procedure are contaminated with oxygen. This paper describes a method and an apparatus for growing oxygen-free silicon bicrystals.

Method of Growing Dash Bicrystals

Dash (10-12) describes a method of growing silicon monocrystals free of dislocations and oxygen. This procedure does not employ the quartz (SiO_2) crucible necessary with the well-known Czochralski method (9). The use of quartz crucibles gives rise to high oxygen content in the pulled crystals. With the Dash method, the crystal is pulled from the molten top of a silicon rod, commonly called the "pedestal." A seed consisting of material of low dislocation density is used. It is tapered at the tip to a diameter of approximately 0.1 mm. The crystal is pulled in an inert argon atmosphere to avoid contamination and oxidation.

For these experiments, a Dash crystal-growing apparatus was constructed. After many perfect silicon monocrystals had been grown, the equipment was used to grow grain boundary crystals with low oxygen content. Silicon material containing grain boundaries was chosen for the seeds, instead of the dislocation-free bars employed in the conventional Dash method.

Crystal grower.—A Lindberg float zone scanner (Model LA-VSE-24 ZR) was converted into a crystal grower. The basic arrangement is shown in Fig. 1.

The quartz tube, L, contains the main components of the crystal grower. The tube (35 mm OD) is

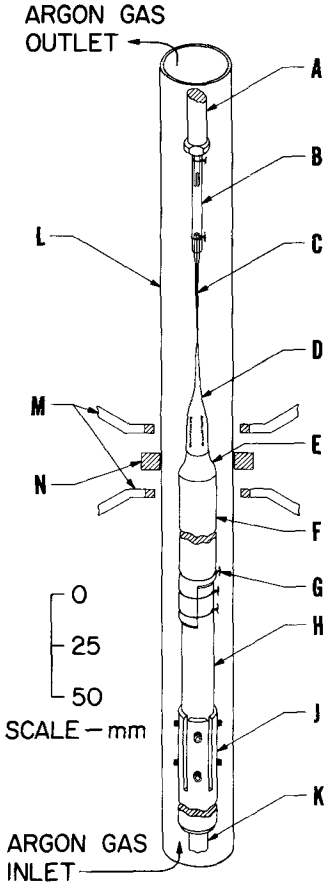

Fig. 1. Schematic drawing of the Dash crystal grower

aligned inside the heating coil, N, and shading coils, M, of the Lindberg RF generator (Model LI-10-C-1, 4MC, 10 KW). During growth, argon gas containing less than 0.1 ppm of oxygen flows through the quartz tube.

The pedestal, F, is connected to the quartz chuck, H, (15 mm diameter, 100 mm length). A slotted steel tube, J, with centering screws supports the quartz rod. The top of the rod is cut to a step shape to fit a corresponding step on the pedestal material. The parts are connected by tantalum wires. One of these wires, G, establishes the coupling of the RF field before the silicon pedestal is heated. The quartz chuck, H, insulates the hot parts of the grower. It also helps to reduce contamination of the pedestal, and improves the ease of aligning the whole assembly. The supporting shaft, K, is mechanically connected to a motor unit. Thus the operator is able to rotate and move all parts, F-K, according to any desired program.

A small quartz tube, B, is used as a "seed holder." It is connected to the elevator shaft A. The crystal, D, is pulled from the melt, E, by moving the seed, C, upward. At the same time it rotates with a constant speed of 6 rpm. The solid liquid interface is kept at a constant level by feeding the pedestal upward to compensate for the removed material.

Preparation of silicon starting material.—Czochralski-grown crystals (25-500 ohm-cm, n-type and 7-15 ohm-cm, p-type) with a diameter of about 18 mm were used as pedestal materials. The top portions of all these rods were tapered to a cone with a SiC-abrasive, while the lower parts were cut to fit the quartz chuck. Subsequently, the pedestal was etched in a solution consisting of 1 part HF (49%) and 3 parts of HNO_3 (70%).

The seed was prepared in the following way: A bicrystal containing a 10.5° grain boundary was grown by the Czochralski method using two seeds disoriented with respect to each other [as described by Mataré and Wegener (13)]. From this crystal a rectangular piece, containing the grain boundary (14) was cut (2 x 2 x 60 mm). It was lapped by hand

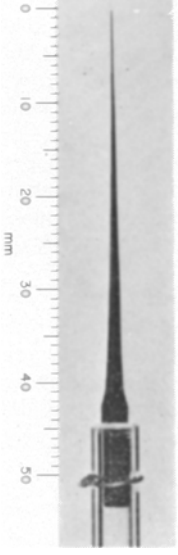

Fig. 2. Etched bi-seed containing a 10.5° grain boundary (diameter of the tip is about 0.1 mm).

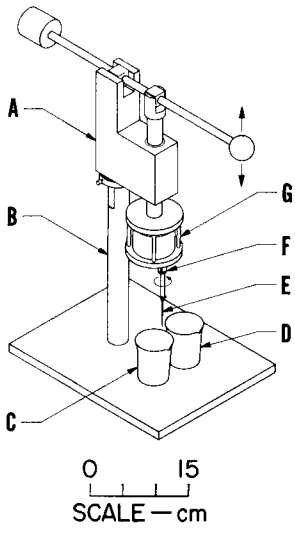

Fig. 3. Etching apparatus

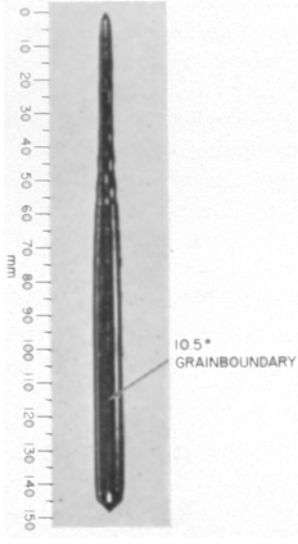

Fig. 4. Oxygen free, 10.5° grain boundary crystal with [100] pull axis.

until the grain boundary was equidistant from both sides parallel to the grain boundary plane. This "bi-seed" was etched to a needlelike shape (see Fig. 2) with the grain boundary still remaining in the center of the tip. The bi-seed must have a small diameter (approximately 0.1 mm) at the tip in order to avoid freezing of the molten silicon on top of the pedestal when the seed is lowered into the melt.

An apparatus for facilitating the etching of the seed crystals was constructed (see Fig. 3). The etching apparatus moves the seed vertically, while simultaneously rotating it at 10 rpm. This way, seed crystals can be etched very accurately to the desired concentric geometry. The etching apparatus is similar to a drill press. The supporting block, A, can be turned about the column, B, so that the seed, E, may be alternatively dipped into the etching solution, C, [1 part HF (49%), 3 parts HNO_3 (70%)] or cooling water, D. The seed is connected to the synchronous motor G, by means of the Teflon chuck, F.

Experimental Results

Figure 4 is a photograph of a Dash grain boundary crystal. The 10.5° grain boundary is seen on the

crystal surface as a fine, sharp line which is not completely parallel to the growth lines. This is caused by inaccurate orientation of the grain boundary with respect to the bi-seed. The crystal is 147 mm long and has a nearly constant diameter of 9 mm over a length of approximately 80 mm. It was grown with a starting pull rate of 4 mm/min and a final pull rate of 1.4 mm/min. The output energy of the RF generator was manually controlled to achieve optimum growing conditions, and the temperature of the molten Si was determined using an optical pyrometer.

Earlier infrared transmission measurements had indicated that Dash crystals grown from unrefined normal Czochralski crystals or from float zone refined silicon bars showed the same absorption peak height at 9μ. The absorption coefficient of all these slices was calculated to be in the order of 0.8 cm^{-1}. This value is known to be the background absorption of silicon itself (15). All measurements were carried out with a Beckman spectrophotometer (Model IR4). Since this instrument has a double-beam arrangement, the test slices cut from crystals grown by the Dash-method could be directly compared with equivalent float zone material placed in the reference path. A slice taken from the bicrystal shown in Fig. 4 was checked in this manner. No oxygen content could be detected by the 9μ absorption line.

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The Effect of Hydrogen Reduction on the Morphology of Copper Oxide Whiskers

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ABSTRACT

A series of closely controlled experiments was conducted to determine the effect of hydrogen reduction on the morphology of oxide whiskers formed on unannealed and preannealed copper. Initial reduction occurred along random sites at the whisker surface. No preferential reduction at the whisker tip was observed. During the reduction cycle, the whiskers collapsed to form small irregularly shaped high-opacity nodes. Some differences were observed in the rate and manner in which the whiskers reduced on the unannealed and preannealed samples which were attributed to initial variations in size and shape of the whiskers. Selected area diffraction analyses of the reduced products revealed that the whiskers changed from CuO to Cu_2O and then to Cu. Cu_2O appeared to form adjacent to the metal surface.

Replica examinations of the oxidized-reduced surfaces when compared with replicas of the original surface revealed considerable surface rearrangement with the formation of subgrain-type structure. The size of the subgrains formed on the preannealed sample appeared to be smaller than that obtained on the unannealed sample. In most cases, the reduced oxide whisker growth products appeared to emanate from subgrain boundary intersections rather than from subboundary interiors.

Unusual growth products resembling needles, blades, serrated blades, etc., have been observed by many workers in the oxidation of metals (1-3). In most cases the growths have been identified by x-ray and electron diffraction techniques to be oxides of the base metal. The whisker shape, in some instances, has been related to the pretreatment given the metal (4) and the environment (5). The exact mechanism